

Mechanical Properties of Nanofilled Polypropylene Composites

Cristina-Elisabeta PELIN (BAN)*^{1,2}, Adriana STEFAN¹, George PELIN^{1,2}, Ion DINCA³, Anton FICAI², Ecaterina ANDRONESCU², Georgeta VOICU²

*Corresponding author

*¹INCAS – National Institute for Aerospace Research “Elie Carafoli”
B-dul Iuliu Maniu 220, Bucharest 061126, Romania

ban.cristina@incas.ro*, stefan.adriana@incas.ro, pelin.george@incas.ro,

²“POLITEHNICA” University of Bucharest, Faculty of Applied Chemistry and
Materials Science

St. Polizu 1-7, 011061, Bucharest, Romania

anton.ficai@upb.ro, ecaterina.andronescu@upb.ro, georgeta.voicu@upb.ro

³AEROSPACE Consulting

B-dul Iuliu Maniu 220, Bucharest 061126, Romania

dinca.ion@incas.ro

DOI: 10.13111/2066-8201.2015.7.2.11

Abstract: *The paper presents a study concerning mechanical performance of thermoplastic nanocomposites based on isotactic polypropylene matrix, nanofilled with montmorillonite modified with quaternary ammonium salt and carboxyl functionalized carbon nanotubes, respectively, added in the same concentration relative to the matrix. The nanofilled and single polymer materials were obtained by simple melt compounding through extrusion process followed by injection molding into specific shape specimens for mechanical testing of the samples. Mechanical properties were evaluated by tensile and 3 point bending tests. In terms of modulus of elasticity, the results showed overall positive effects concerning the effect of nanofiller addition to the thermoplastic polymer. The fracture cross section of the tested specimens was characterized by FT-IR spectroscopy and SEM microscopy.*

Key Words: *nanoclay, carbon nanotubes, polypropylene nanocomposites, Young's modulus, tensile strength, flexural strength*

1. INTRODUCTION

Polymer nanocomposites have gained interest in the last decades due to the attractive properties of nanostructured fillers, and their ability to enhance the matrix performance when added in low contents (1- 5%), improvements comparable to those achieved by conventional loadings (15- 40%) of traditional fillers [1].

This new class of multifunctional materials found applications in a wide variety of fields, from microelectronics to aeronautic and aerospace industry [2].

Owned to their good balance between properties, low density, corrosion resistance, facile processability and low cost [3, 4], polyolefins represent one of the most versatile class of polymeric matrices.

Nanofilled isotactic polypropylene (PP) nanocomposites can be obtained through several processing methods, melt mixing, solution casting and in situ polymerization, among them, melt mixing having some major advantages as it combines high speed and simplicity

with the absence of solvents and contaminants [5]. Carbon nanotubes and layered silicates represent two of the most promising reinforcement agents, due to their properties that can provide the final composite special characteristics from mechanical, thermal or electrical point of view. Studies show that lower nanofiller contents lead to enhanced mechanical properties [6-9].

There are studies that illustrate the achievement of better dispersion and exfoliation degree of PP/modified montmorillonite nanocomposites by extrusion processing vs. melting intercalation [6].

Overall, literature studies attest significant Young's modulus increase for montmorillonite contents up to 3% by weight, followed by a lower increase trend for contents higher than 4% [6]. Acid modified multiwalled carbon nanotubes disperse well in polypropylene matrix, presenting a 16 % increase of tensile strength with MWCNT content up to 2 % by weight, while a 17% increase was noticed when adding 4% acid treated MWCNT from 29 MPa for simple PP to 34 MPa for nanofilled PP [7]. Thiebaud [10] investigated mechanical characteristics of PP/MWCNT with 1, 2, 4 and 8% nanotubes content, noticing an increase of Young's modulus and a significant decrease in tensile strength at fracture with content increase.

The study presents the characterization of isotactic polypropylene filled with carboxyl functionalized MWCNT and quaternary ammonium salts modified montmorillonite (Cloisite30B) obtained through the simple melt extrusion technique.

The experimental study aim was to evaluate the mechanical properties of this type of materials obtained through simple melt mixing at certain parameters considered to be optimum for a good homogenization.

The results show an improvement of the tensile and flexural strength and modulus when adding nanofiller. In the case of MWCNT, the nanocomposites presented higher stiffness compared to simple PP and Cloisite 30B based PP. Cloisite 30B improvements are lower than the ones obtained with MWCNT, probably due to the nature of the modifying agents of the montmorillonite that does not favor an optimum dispersion.

2. EXPERIMENTAL SECTION

2.1 Materials

The matrix used for the nanocomposite obtaining was isotactic polypropylene homopolymer (TIPPLEN H 949 purchased from Bastplast SRL) with 45 flow index. The nanofillers were added in 4% by weight relative to the matrix.

The carbon nanotubes used as fillers were multi-wall carbon nanotubes functionalized with carboxylic groups (MWCNT- COOH), purchased from Chengdu Organic Chemicals Co. Ltd having 95% purity, outer diameter of 10-20 nm, 10-30 μm length, 233 $\text{m}^2 \cdot \text{g}^{-1}$ special surface area, and approximately 2.1 $\text{g} \cdot \text{cm}^{-3}$ density.

The second nanofiller was Cloisite 30B- montmorillonite modified with quaternary ammonium salt (methyl tallow bis-2-hydroxyethyl ammonium chloride), purchased from Southern Clay Products- USA, with a density of 1.98 $\text{g} \cdot \text{cm}^{-3}$ and up to 2% moisture content. Cloisite 30B was dried 12 hours at 80°C before processing.

2.2 Nanocomposite synthesis

The nanocomposite samples were obtained by direct melt compounding using a twin screw extruder (Leistritz LSM 3034- with a 34 mm diameter screw). The polypropylene (PP)

pellets and nanofiller powders were mixed with gradual temperature increase on the ten heating areas of the extruder.

The extrusion was carried out on temperature profile from 150- 170°C, using a 250 rpm feed speed rate and 220 rpm screw rotation speed.

Afterwards the filaments were cooled in water bath, chopped and dried at 80°C. The extruded pellets were injection molded to obtain test specimens for the mechanical tests.

Temperatures for injection were between 165-185°C from the feeding area to the injection nozzle.

Double screw extruder is more appropriate equipment than the one screw extruder, for the production of nanocomposites based on PP and carbon nanotubes as it is more likely to ensure a better homogenisation and an optimum pathway through the extruder [11, 12]. Optimum screw speed is required for dispersion improvement. Too high speed rates can generate mechanical degradation of the final nanocomposite while too low speed rates could be insufficient for the nanofiller homogenization in the matrix [13].

Relative to the matrix, both carboxyl carbon nanotubes and modified montmorillonite were added in 4 % by weight content, as higher contents favor agglomeration, and also lead to non-viable materials from economic point of view.

2.3 Physicochemical and morphological characterization

The nanocomposites were subjected to spectroscopy analysis using Thermo iN10 MX Mid Infrared FT-IR Microscope and scanning electron microscopy using HITACHI S2600N microscope.

2.4 Mechanical Testing

The simple polymer and 4% nanoadditivated specimens were subjected to mechanical tests in order to evaluate their mechanical strength and stiffness in terms of tensile and flexural resistance.

The tests were performed on INSTRON 5982 mechanical test machine, according to SR EN ISO 527-2 for tensile test, using 50 mm·min⁻¹ tensile rate, and 1A type specimens and SR EN ISO 178 for 3-point bending test, using 2 mm·min⁻¹ speed of test, rectangular specimens at nominal span length (depending on sample thickness). For both sets of mechanical tests, a minimum of 5 specimens per sample was used, and the resulting data were calculated using Bluehill 3 software.

2.5 Density measurement

The density evaluation was performed using the classical method of the ratio between mass and volume of accurate dimensions samples.

An accurate analytical balance was used for sample mass measuring. The volume was measured using displacement method.

3. RESULTS AND DISCUSSION

3.1 FTIR spectroscopy

Prior to FTIR analysis, the samples were pressed, with the fracture cross-section upwards in order to visualize the peaks characteristic to the bulk nanocomposites composition. The analysis was conducted in ATR (Attenuated Total Reflectance) mode. Fig. 1 presents the spectra of the simple polypropylene sample in comparison with the nanofilled samples.

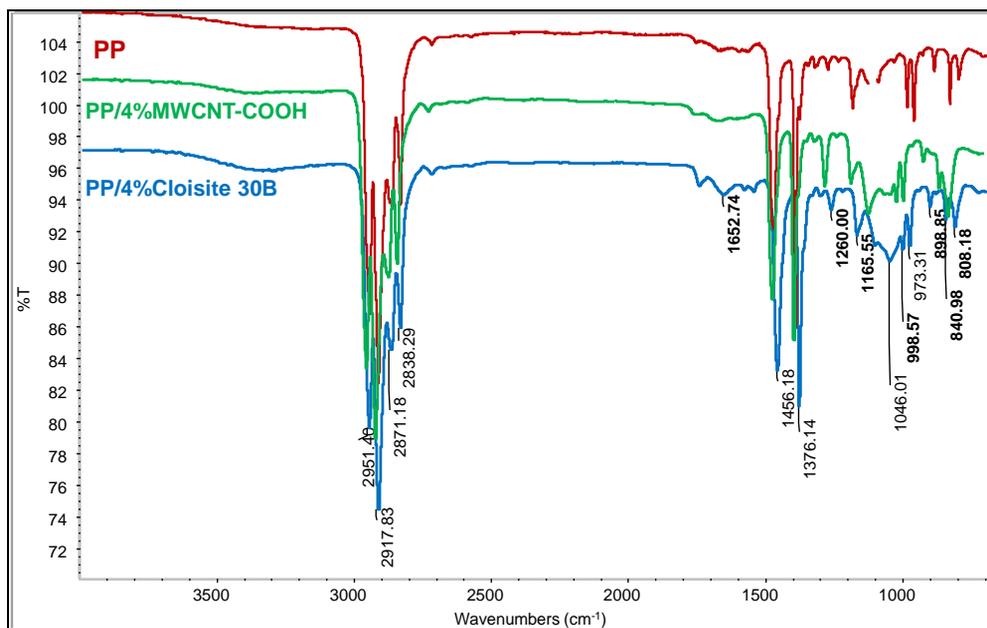


Fig. 1 – FTIR spectra of the simple and nanofilled polypropylene

In the spectra of Cloisite 30B based nanocomposites, the characteristic peaks of the nanofiller can be observed: stretching vibration of -OH from silicatic groups and the presence of water [14] at around 2920, 2850 and 1470 cm^{-1} , stretching vibration of Si-O-Si at around 1050 cm^{-1} .

Bending vibration of Al-OH-Al from montmorillonite at 920 cm^{-1} [15, 16] is overlaid by -CH_3 stretching and C-H bending vibrations from polypropylene structure [17]. Likewise in the region between $2800\text{-}2950\text{ cm}^{-1}$, the peaks corresponding to the nanoclay overlay with the intense peaks characteristics to the polymer.

When compared to PP, the differences appear at 1046 cm^{-1} where Si-O-Si from the Cloisite 30B silicate generates a more intense peak [18] and at 1653 cm^{-1} value at which the signal intensity increases, fact that is generated by the bending vibration of montmorillonite intermediate layer [19].

The increase in intensity of the peaks at 1545 și 1740 cm^{-1} could be due to the eventual oxidation processes that could have occurred during materials processing (high temperature during injection stage), that could be assigned to some degradation processes suffered by the matrix. There are studies that discuss the fact that simple Cloisite 30B powder decomposition starts around $174\text{ }^\circ\text{C}$ [20], through degradation of organic groups from the modifying agent (quaternary ammonium salts) [18].

In the spectra of MWCNT based nanocomposites, there are some differences in $1000\text{-}1100$ and $1500\text{-}1750\text{ cm}^{-1}$ domains probably due to the interaction of the matrix with the carbon nanotubes [21].

In the region $1000\text{-}1100\text{ cm}^{-1}$ the signals become more intense compared to the pure PP, probably due to the presence of functionalized MWCNT [22], the intensity increase of 1078 cm^{-1} peak resulting from stretching vibration of C-O [23].

The weak peak at approximately 1738 cm^{-1} can be due to the stretching vibration of C=O from COOH group [23], while modifications at 1550 cm^{-1} , may be connected to the presence of functionalized nanotubes [24].

3.2 SEM Analysis

SEM microscopy analysis were performed in the fracture cross-section of the materials, so that the nanofiller presence could be evidenced, as the cross-section is strongly influenced by the nature of nanofiller, presenting visible edges and cracks prior to the tensile test fracture.

At 500 X magnification level a good dispersion of the MWCNT can be noticed, as well as the fracture initiation sites. The non-uniformities observed in the Cloisite30B based sample could be one of the reasons for slightly lower mechanical properties improvements for these samples compared to the MWCNT ones.

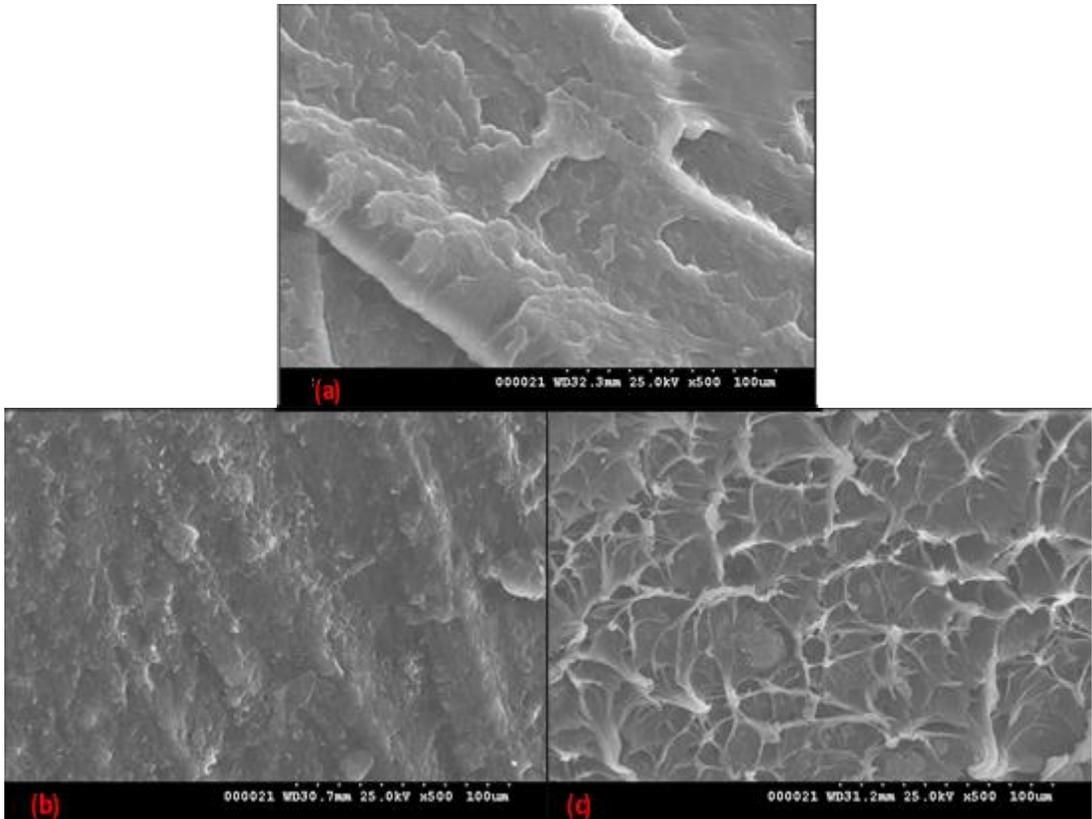


Fig. 2 – SEM images of PP based nanocomposites compared to simple PP, at x500 magnification level: (a) PP, (b) PP/4% Cloisite30B, (c) PP/4% MWCNT-COOH

3.3 Mechanical testing

Tensile test

Tensile test results highlighted the differences in tensile strength and Young's modulus induced by each of the two types of nanofillers added in the same concentration to the matrix. The test was performed according to SR EN ISO 527-2 standard specifications [25], for tough materials without yield point class. Tensile strength is calculated as maximum tensile stress sustained by the specimen during the test (tensile stress at tensile strength). To obtain Young's modulus, the software calculated the slope of each stress-strain curve, using two specified strain values, according to standard [25]. For each sample, the values outside the mean domain were eliminated. Fig. 3 presents the stress-strain curves of the replicas of the mediated specimens corresponding to each sample.

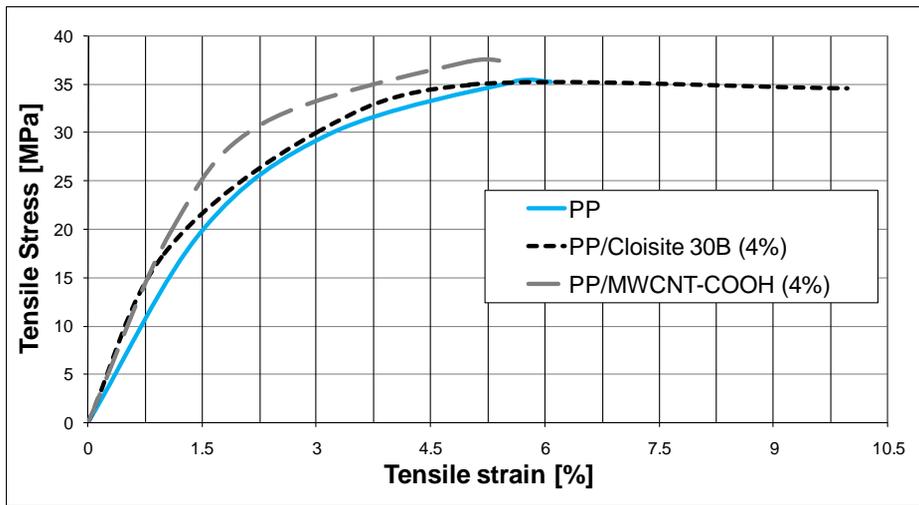


Fig. 3 – Stress- strain curves corresponding to the PP based nanocomposites

In the case of MWCNT-COOH, the addition of nanofiller does not induce significant changes in tensile strain (elongation during tensile testing) while the addition of Cloisite30B increases the tensile strain value up to approximately 10%. This means that the Cloisite30B based PP sample can experience a larger amount of strain before failure during tensile testing, proving that adding Cloisite 30B results in a more ductile material. This observation is in accordance with the slightly lower strength and modulus compared to PP/MWCNT (Table 1), as elongation is inversely proportional to tensile strength, and modulus. As PP/MWCNT showed higher strength and modulus, it obviously elongated less under stress.

Flexural test

As polypropylene is known to be a flexible material, 3-point bending test was carried out until conventional deflection (calculated as 1.5 of the specimen thickness), and not until break. Flexural strength is represented by flexural stress at conventional deflection [26]. It is worth mentioning that the flexural modulus represents an approximate value of the Young's modulus of elasticity.

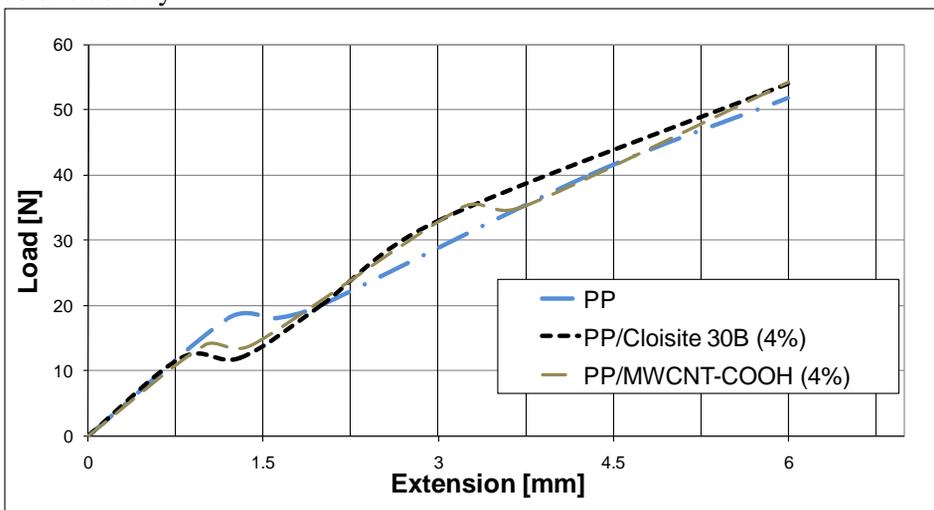


Fig. 4 – Load- extension curves corresponding to the simple and nanofilled PP composites

Mechanical tests results summarized in Table 1, show that the nanocomposites presented superior characteristics compared to the base PP, the increase was more significant regarding tensile behaviour, especially Young's modulus, while maintaining a low density.

Table 1 – Mechanical characteristics and density of simple and nanofilled PP

PP based materials	Density (g·cm ⁻³)	Tensile stress at tensile strength (MPa)	Young's modulus (MPa)	Flexure stress at Tensile Strength (MPa)	Young's flexure strain (MPa)
PP	0.87	35.3	2026	32.5	1439
PP/ Cloisite30B	0.90	36.2	2256	33.6	1505.3
PP/ MWCNT-COOH	0.93	37.4	2414	33.6	1575.2

The nanofilled PP materials maintained their low density characteristic to this polymer, presenting an insignificant increase, less than 8% for the MWCNT and less than 4 % increase for the Cloisite 30B nanocomposite, compared to the simple PP. Nevertheless, the mechanical properties showed improvements.

Adding 4% by weight MWCNT-COOH generated an increase in tensile modulus of approximately 20% compared to the simple PP, while adding 4% Cloisite 30B presented 12% larger value compared to PP. In terms of flexural modulus, the MWCNT nanocomposite presented an increase by 10%, while Cloisite 30B presented an average value increased by 5% compared to PP.

These results could be determined by a high degree of dispersion of the nanofiller in the matrix and prove that adding MWCNT-COOH lead to stiffer materials, as tensile modulus is a measure of a material's stiffness (rigidity) [27].

The fact that the addition of Cloisite 30B did not induce significant improvements in terms of mechanical properties could be due to the fact that montmorillonite needs a higher enthalpy to overcome entropic disadvantages.

Optimum enthalpy is obtained when the polymer-montmorillonite interactions are stronger than between modifying agent-montmorillonite. For most polar polymers, common modifying agents as alkyl ammonium salts are efficient, but for non-polar PP the modifying agent has to have the same non-polar aliphatic nature as PP, the enthalpy value being too low for a good dispersion [6]. The increase values for tensile and flexural strength were in the range of 3- 6% in both nanofilled composites.

This fact could be due to the eventual, filler–filler agglomerates that are likely to act as stress-concentrating sites [28].

Melt extrusion uses mechanical dispersion, which could be insufficient to uniformly disperse the nanosized particles, even at optimum parameters. The nanometric dimensioned fillers generally require dispersion in polymers using ultrasonication.

However, this method can be applied using dissolution of the matrix in an adequate solvent, technique that has some major disadvantages compared to the simple melt technique, as the nature of PP makes it insoluble in most of organic solvents, leading to difficult processing, and most importantly it requires large solvent quantities that lead to economically and environmentally non- profitable processing.

4. CONCLUSIONS

The study presents the mechanical characterization of isotactic polypropylene filled with carboxyl functionalized MWCNT and quaternary ammonium salts modified montmorillonite

(Cloisite 30B) prepared through the simple and quick way of melt extrusion technique. The results show an improvement of the mechanical strength and modulus, especially regarding Young's modulus of elasticity that showed up to 20% higher value for carbon nanotubes based PP. The nanocomposites maintained their low density advantages showing a minor increase when adding 4% nanofiller.

This observation along with the mechanical improvements shows that this kind of materials could have potential as light and strong solutions for applications in fields where mechanical strength and stiffness are required.

The experimental research will continue focusing on achieving a chemical interaction between the matrix and the nanofillers, to increase matrix- filler adhesion through improved chemical compatibilization by grafting the polypropylene with different agents such as maleic anhydride or methylstyrene [6]. This fact can lead to nanocomposites with even higher mechanical properties.

ACKNOWLEDGMENT

Some data described in the study was presented at the International Conference of Aerospace Sciences "Aerospatial 2014" 18 - 19 September, Bucharest, Romania, the present paper discussing a more in depth analysis of the mechanical properties.

This work has been funded by Romanian Ministry of Education through the PN-II-PT-PCCA- 168/2012 project: "Hybrid composite materials with thermoplastic matrices doped with fibres and disperse nano fillings for materials with special purposes" and by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132397.

REFERENCES

- [1] K. I. Winey and R. A. Vaia, Polymer Nanocomposites, *MRS Bulletin*, vol. **32**, no. 4, pp. 314-322, 2007.
- [2] F. Hussain, M. Hojati, M. Okamoto and R. E. Gorga, Polymer-matrix nanocomposites, processing, manufacturing, and application: an overview, *Journal of Composite Materials*, vol. **40**, no. 17, pp. 1511–1565, 2006.
- [3] M. Mihaela and A. Olaru, *Handbook of polyolefins*, Marcel Dekker Inc., New York.
- [4] M. Dolgovskij, P. Fasulo, F. Lortie, Christopher W. Macosko, R. Ottaviani and W. Rodgers, Effect of mixer type on exfoliation of polypropylene nanocomposites, *Proceedings of the 61st Annual Technical Conference (ANTEC)*, Nashville, USA, 2003.
- [5] E. Logakis, E. Pollatos, Ch. Pandis, V. Peoglos, I. Zuburtikudis, C.G. Delides, A. Vatalis, M. Gjoka, E. Syskakis, K. Viras and P. Pissis, Structure–property relationships in isotactic polypropylene/multi-walled carbon nanotubes nanocomposites, *Composites Science and Technology*, vol. **70**, no. 2, pp. 328-335, 2010.
- [6] E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu, and T. C. Chung, Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties, *Chem Mater*, vol. **13**, no. pp. 3516-3523, 2001.
- [7] M. Awang, W-V. Hor, E. Mohammadpour, M. Z. Abdullah and F. Ahmad, Functionalization and Characterization of Carbon Nanotubes/Polypropylene Nanocomposite, *World Academy of Science, Engineering and Technology*, vol. **5**, no. 10, pp. 352-356, 2011.
- [8] D. Bikiaris, A. Vassiliou, K. Chrissafis, K.M. Paraskevopoulos, A. Jannakoudakis and A. Docoslis, Effect of acid treated multi-walled carbon nanotubes on the mechanical, permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene, *Polymer Degradation and Stability*, vol. **93**, no. 5, pp. 952-967, 2008.
- [9] S. P. Bao and S.C. Tjong, Mechanical Behaviour of Polypropylene/Carbon Nanotube Nanocomposites: The effects of loading rate and temperature, *Material Science and Engineering A*, vol. **485**, no. 1-2, pp. 508–516, 2007.

- [10] F. Thiebaud and J. C. Gelin, Multiwalled Carbon Nanotube/Polypropylene Composites: Investigation of Melt Processing by Injection Molding and Analysis of the Resulting Mechanical Behaviour, *Int J Mater Form*, vol. **2**, no. 1, pp. 149-152, 2009.
- [11] G. Horvath and Cs. Varga A. Szentés, Mechanical Properties of Polypropylene/Multi Walled Carbon Nanotube Composites, *Hungarian Journal of Industrial Chemistry*, vol. **38**, no. 1, pp. 67-70, 2010.
- [12] C. Y. Lew, M. Claes and F. Luizi, *The Influence of Processing Conditions on the Electrical Properties of Polypropylene Nanocomposites Incorporating Multiwall Carbon Nanotube*, Nanocyl S.A., Sambreville, Belgium
- [13] T.Y. Hwang, H. J. Kim, Y. Ahn and J.W. Lee, Influence of twin screw extrusion processing condition on the properties of polypropylene-multi-walled carbon nanotube nanocomposites, *Korea-Australia Rheology Journal*, vol. **22**, no. 2, pp. 141-148, 2010.
- [14] C. Saha, T. K.Chaki and N. K. Singha, Synthesis and Characterization of Elastomeric Polyurethane and PU-Clay Nanocomposites Based on an Aliphatic Diisocyanate, *Journal of Applied Polymer Science*, vol. **130**, no. 5, pp. 3328-3334, 2013.
- [15] G. Malucelli, R. Bongiovanni, M. Sangermano, S. Ronchetti and A. Priola, Preparation and characterization of UV-cured epoxy nanocomposites based on o-montmorillonite modified with maleinized liquid polybutadienes, *Polymer*, vol. **48**, no. 24, pp. 7000-7007, 2007.
- [16] P. A. Tarantili, *Composites of Engineering Plastics with Layered Silicate Nanofillers: Preparation and Study of Microstructure and Thermomechanical Properties*, in Nanocomposites and Polymers with Analytical Methods, Cuppoletti J (Ed.), InTech, 2011.
- [17] I. Karakan and H. Bensli, The use of infrared-spectroscopy technique for the structural characterization of isotactic polypropylene fibres, *Journal of Textile & Apparel* vol. **21**, no. 2, pp. 116-23, 2011.
- [18] S. Mohamadi and N. Sharifi Sanjani, *Studies on PEBAX/organoclay nanocomposites by meltintercalation process: Effect of organoclay surface e-Polymers*, vol. **135**, 2009.
- [19] P. Kumar, *Development of Bio-nanocomposite Films with Enhanced Mechanical and Barrier Properties Using Extrusion Processing*, [PhD] Thesis, Faculty of North Carolina State University Food Science Department, 2009
- [20] A. Leszczynska and J. Njuuna K. Pieliowski. *Mechanism of thermal degradation of layered silicates modified with ammonium and other thermally stable salts*. in *Thermally Stable and Flame Retardant Polymer Nanocomposites*, Mittal V (Ed.), Cambridge, UK Cambridge University Press, 2011
- [21] L. V. Diyakon, O. P. Dmytrenko, N. P. Kulish, Yu. I. Prylutsky, Yu. E. Grabovskiy, N. M. Belyy, S. A. Alekseev, A. N. Alekseev, Yu. I. Sementsov, N. A. Gavrylyuk, V. V. Shlapatskaya, L. Valkunas, R. Ritter and P. Scharf, Radiation damage of isotactic polypropylene composites with multi-walled carbon nanotubes *Functional Materials*, vol. **15**, no. 2, pp. 169-174, 2008.
- [22] V.T. Le, C. L. Ngo, Q. T. Le, T. T. Ngo, D. N. Nguyen and M. T. Vu, Surface modification and functionalization of carbon nanotube with some organic compounds, *Advances in Natural Sciences: Nanoscience and Nanotechnology* vol. **4**, no. 3, pp., 2013.
- [23] S-C. Her and C-Y. Lai, Dynamic Behavior of Nanocomposites Reinforced with Multi-Walled Carbon Nanotubes (MWCNTs), *Materials*, vol. **6**, no. 6, pp. 2274-2284, 2013.
- [24] K. Mishra and P. L. Nayak C.R. Biswal, Synthesis and Characterization of Modified Multi-Walled Carbon Nanotubes Filled Thermoplastic Natural Rubber Composite, *Middle-East Journal of Scientific Research*, vol. **18**, no. 2, pp. 168-176, 2013.
- [25] International Organization for Standardization, SR EN ISO 527-2- Determination of tensile properties of plastics, Test condition for moulding and extrusion plastics, 2000.
- [26] International Organization for Standardization, European Standard EN ISO 178- Plastics - Determination of flexural properties, 2003.
- [27] B. K. Sridhara S. R. Katti, L. Krishnamurthy and G. L. Shekar, Mechanical Behaviour of MWCNT Filled Polypropylene Thermoplastic Composites, *Indian Journal of Advances in Chemical Science* vol. **2**, pp. 6-8, 2014.
- [28] S.A. Girei, S. P. Thomas, M. A. Atieh, K. Mezghani, S.K. De, S. Bandyopadhyay and A. Al-Juhani, Effect of -COOH Functionalized Carbon Nanotubes on Mechanical, Dynamic Mechanical and Thermal Properties of Polypropylene Nanocomposites, *Journal of Thermoplastic Composite Materials*, vol. **25**, no. 3, pp. 333-350, 2012.